Available online at www.sciencedirect.com
SCIENCE DIRECT®
Renewable and Sustainable Energy Reviews
9 (2005) 395–408
RENEWABLE & SUSTAINABLE ENERGY REVIEWS
www.elsevier.com/locate/rser

Progress and problems in hydrogen storage methods

Li Zhou*

High Pressure Adsorption Laboratory, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

Received 19 May 2004; accepted 19 May 2004

Abstract

A technique of hydrogen storage has to meet the DOE criterion for the volumetric and gravimetric density of the stored hydrogen and the reversibility criterion for the charging/discharging processes. There are basically five candidate methods that have attracted the common interest: compression, liquefaction, physisorption, metallic hydrides, and complex hydrides. An overview was given for the storage methods available today with respect to the progress made recently and problems still there.

Keywords: Hydrogen; Storage; State; Overview

Contents

* Tel./fax: +86-22-87891466.
E-mail address: zhouli-tju@eyou.com.

doi:10.1016/j.rser.2004.05.005

1. Introduction

Hydrogen is shown to be the future fuel from the point of view of human fuel evolution. The fuel evolution experienced the history from coal through petroleum to natural gas following the direction of increasing the content of hydrogen, therefore, it must finally reach the destination of pure hydrogen. Every step of the fuel evolution initiated a progress in human civilization, therefore, the large-scale utilization of hydrogen fuel will certainly elevate the human civilization to a higher horizon. Hydrogen is the cleanest fuel, and has a heating value three times higher than petroleum. However, it is not a natural source, but a man-made fuel; therefore, hydrogen bears a manufacture cost, which made it costing three times higher than the petroleum products. Therefore, any method of storage is not allowed to considerably increase the cost of hydrogen fuel. There are still problems in the realization of the renewed hydrogen from water, but the market supply and the cost of hydrogen do not constitute the bottleneck of hydrogen vehicles today although the hydrogen used presently may not be renewed. There is only one bottleneck for the hydrogen vehicle program, the storage of hydrogen. Just think about as large as 49 m^3 that 4 kg hydrogen occupies, which is required for a practical driving distance, one can imagine how difficult is the job of hydrogen storage. Storage basically implies to reduce the enormous volume of the hydrogen gas. The reversibility of the hydrogen uptake and release excludes all covalent hydrocarbon compounds as hydrogen carriers because the hydrogen is only released from the compounds if being heated to temperatures above 800 °C. The methods of interest include compression, liquefaction, physisorption, metallic hydrides, and complex hydrides, which are commented with respect to the technical state and the viability in future application.

2. Compression

It might be the simplest way to store hydrogen in a cylinder of pressure up to 20 MPa, but the energy density is too low to satisfy the fuel demand of driving practice. About four times higher pressure is needed to meet the driving purpose, however, such industrial cylinders have not been commercially available. Industry sets up a goal to manufacture cylinders capable of withstanding pressure up to 70 MPa with a weight 110 kg to reach a gravimetric density 6%; and volumetric density 30 kg/m^3. The hydrogen density as such is remarkably lower than the cryoadsorption method, and the high cost of compression and the cylinder might hinder the method to be accepted commercially. The isothermal

compression of hydrogen from 0.1 to 80 MPa consumes energy 2.21 kW h/kg, but much higher energy would be consumed in a real process as the case of liquefaction. A report from Linde Company estimates the cost of compressed H_2 is much higher than the cost of liquid hydrogen. It seems, therefore, this method is not likely to be used in the future. Furthermore, the safety of pressurized cylinders is of big concern especially in the densely populated regions.

3. Liquefaction

This method faces two challenges: the efficiency of the liquefaction process and the boil-off of the liquid. The theoretical work necessary to liquefy hydrogen gas of room temperature is 3.23 kW h/kg, but the technical work is about 15.2 kW h/kg, which is almost half of the lower heating value of hydrogen [1]. Gasification of liquid hydrogen inside the cryogenic (21.2 K) vessel is an inevitable loss even with a perfect insulation technique. The exothermic reaction of the conversion from ortho- to para-hydrogen provides a heat source of the gasification. The heat of conversion is 519 kJ/kg at 77 K, and 523 kJ/kg at temperatures lower than 77 K, which is greater than the latent heat of vaporization (451.9 kJ/kg) of normal hydrogen at the normal boiling point. The critical temperature of hydrogen is very low (33.2 K), above which liquid state cannot exist. Therefore, liquid hydrogen can only be stored in an open system otherwise the pressure in a closed system can be as high as 1000 MPa at room temperature. So, the boil-off of liquid means the emission of H_2 into the atmosphere. The relatively large amount of energy necessary for liquefaction and the continuous boil-off of liquid limit this storage system to utilizations where the cost of hydrogen is not an important issue and the hydrogen is consumed in a rather short time, e.g. air and space applications.

4. Physisorption

4.1. The fundamentals

The storage of hydrogen can rely on physisorption because the adsorbed gas can be released reversibly. There are different mechanisms of adsorption depending on the geometry of the adsorbent and the temperature of adsorption. Multilayer mechanism functions if the adsorption happens on an open surface and volume filling would happen in a pore narrower than 2 nm. Capillary condensation could happen in a pore larger than 2 but smaller than 50 nm. Adsorption in a pore larger than 50 nm is the same as that on open surfaces. However, all the mechanisms here mentioned assume the possibility of condensation of the adsorbed adsorbates. Such possibility does not exist at above-critical temperatures; therefore, a different mechanism of adsorption must assume. There is only one mechanism for the adsorption of supercritical gases on any kind of adsorbents, that is the monolayer surface coverage. The single mechanism corresponds to the single type of isotherms of supercritical adsorption. This argument can be proved on considering the well-known BET theory of adsorption [2]. According to BET, the first molecular layer of

adsorbate is fixed on the solid surface due to the interaction between gas and solid. When the surface was completely covered with a layer of adsorbate, more gas molecules would be adsorbed above the first layer due to the interaction between the same species of adsorbate molecules forming the second layer, and so on for the subsequent layers. The interaction force received by the first layer molecules is, thus, different from that received by the second and subsequent layers. This difference must be reflected in the heat of adsorption of different layers. The experiment with nitrogen and carbon black [3] showed that the heat of adsorption of the first layer is 11–12 kJ/mol (0.11–0.12 eV) and it drops to the latent heat of condensation, 5.56 kJ/mol (0.058 eV) in the subsequent layers. Obviously, the subsequent layers from the second cannot exist at above-critical temperatures, otherwise a classical law of physics, i.e. gas cannot be liquefied at above-critical temperatures no matter how high pressure applied, would be false.

The monolayer adsorbate is itself fixed by a weak interaction; therefore, significant physisorption is only observed at relatively low temperatures. Shown in Fig. 1 is the linear variation of the logarithm of the saturation adsorption of hydrogen on activated carbon with temperature [4].

In summary, the physisorption of supercritical gases follows two basic rules: the monolayer adsorption mechanism, and the exponential decrease of adsorption with the increasing temperature. It follows that the adsorption capacity of hydrogen on a material depends on the specific surface area of the material and that higher temperatures will lower the adsorption capacity. The total storage capacity in a porous solid is, however, not only the adsorption capacity, but also the sum of contributions due to adsorption on solid surface and that due to compression in the void space [5].

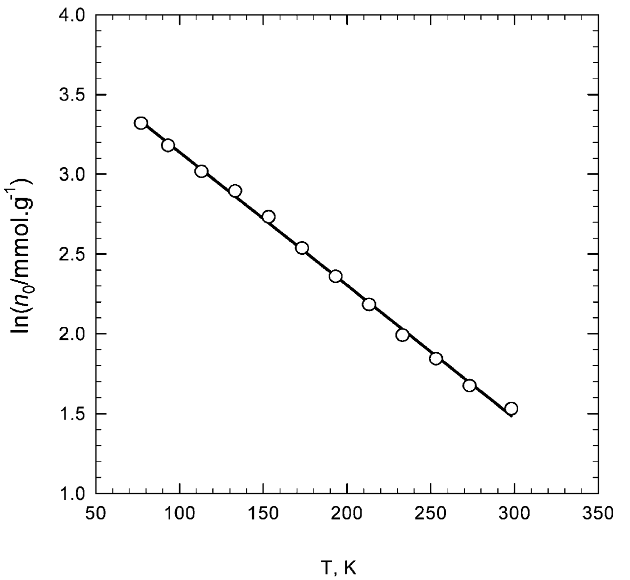


Fig. 1. Variation of the saturation adsorption with temperature [4].

4.2. Hydrogen storage in nanostructure carbons

Dillon et al. [6] presented the first report on hydrogen storage in carbon nano-tubes and triggered a world-wide tide of research on carbon nanotubes. However, their result was rebutted lately [7,8]. The succeeding experiments on carbon nano-tubes were carried out with different methods under various conditions. Samples are usually very small and often not well characterized. Some results of rather high storage capacity were later shown due to the faults of experiment. About 40 references reporting the hydrogen uptake capacity measured on nanostructure carbons have been looked up in CA until the end of 2003 [9–47]. The numbers are shown in Fig. 2, where the triangle dots are the data for low temperatures (around 80 K), and the circles are the data for ambient temperatures. The low temperature capacity is supposed to be one order of magnitude higher than that for ambient temperature, but the triangles are totally buried in the circles indicating a fact that serious uncertainty is involved in the data reported for the hydrogen uptake capacity of carbon nanotubes. The reports from GM and Sony companies [42,43] deserve special attention because they are the potential buyers of the technology. The former claimed that any reported capacity of higher than 1 wt% is due to experimental errors, and the latter reported a capacity of only 0.3 wt%.

Some authors explained their rather high hydrogen uptake capacity at ambient temperature with the possibility of hydrogen liquefaction inside nanotubes. There are two counter arguments against the explanation. First of all, hydrogen condensation at ambient temperature is absolutely impossible no matter where it locates. The fact that liquid

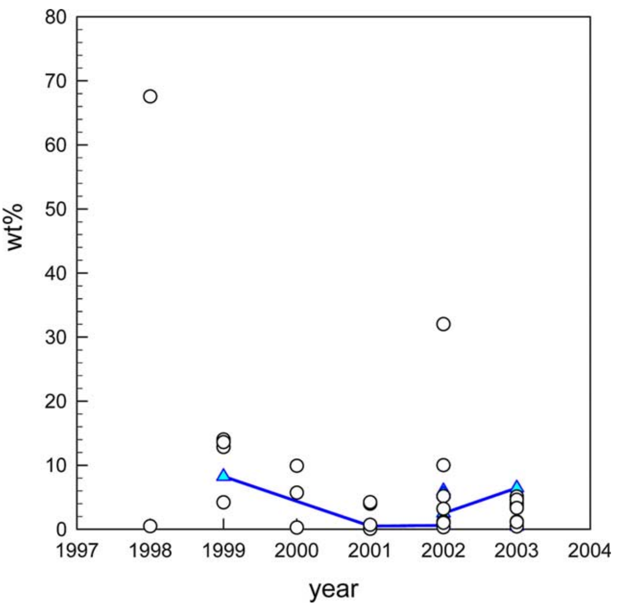


Fig. 2. The measured hydrogen uptake capacity of references until the end of 2003 [9–47].

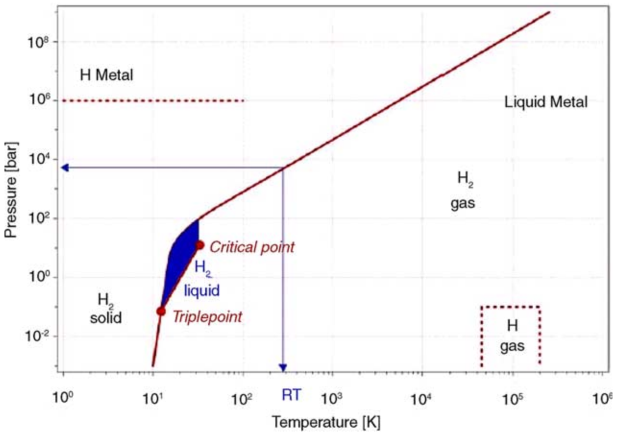


Fig. 3. Primitive phase diagram for hydrogen [48].

hydrogen can never exist beyond the narrow temperature range of 21.2–33 K is indicated in Fig. 3, which is the primitive phase diagram for hydrogen [48]. In addition, molecular dynamics simulation showed that condensation did not happen even for a pressure as high as 35 GPa inside a simulated single wall carbon nanotube with a diameter 0 683 nm [49]. Second, whether hydrogen molecules can or not enter the interior space of nanotubes is a question. Should the strengths of the adsorption potential at the ends and the exterior surface of a nanotube are equal, the ratio of the probabilities for a hydrogen molecule to enter the tube or to be adsorbed on the exterior surface must equal the ratio of areas of the tube openings to the exterior surfaces, which is usually very small. Besides, the adsorption potential of the exterior surface renders nanotubes interacting each other and form bundles, which together with the adsorption of hydrogen molecules on the exterior surfaces increase considerably the transportation resistance of hydrogen to the openings. Therefore, it is difficult for the hydrogen molecules to be adsorbed on the interior surface of carbon nanotubes unless there is a ‘black hole effect’ at the ends of nanotubes.

Practical way to explore what really happens during the adsorption of hydrogen in nanotubes is to observe the behavior of the adsorption isotherms. Unfortunately, no much information about isotherms was available in literature. Therefore, five adsorption isotherms for 233–318 K [50] and three isotherms for 77 K [47] were collected by the author and are shown in Fig. 4. The isotherm 77 K-1 is for the powder sample without heat treatment, 77 K-2 is after the treatment of heating the powder at 400 °C for 1 h in nitrogen atmosphere, and 77 K-3 is for the pellets of nanotubes. It is shown that the uptake capacity at 77 K is remarkably higher than for higher temperatures, and all isotherms show typical feature of supercritical adsorption. The isotherm behaves like type-I if the adsorption is far ahead the saturation, and a maximum appears at some pressure, after which it drops down with the increasing pressure. The heat of adsorption was evaluated based on the isotherms for 233–318 K. It is −1.8 kJ/mol, only one-forth of that on activated carbon [51]. The model for supercritical adsorption [52–54] was applied for the three isotherms at 77 K, and the adsorption predicted by the model was marked with curves. Apparently, the model fits the isotherms very well. It is concluded, therefore, the uptake of hydrogen by carbon

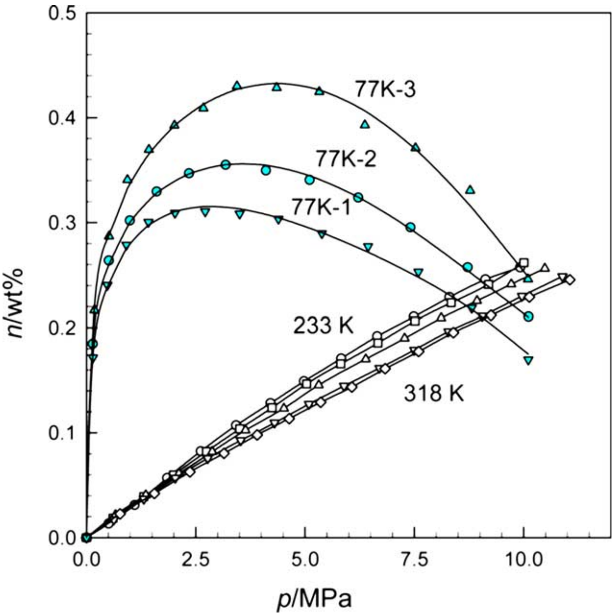


Fig. 4. Adsorption isotherms of H_2 on multiwalled carbon nanotubes [47,50].

nanotubes follows the rules of supercritical adsorption. Therefore, the specific surface area of carbon nanotubes and the temperature of adsorption control the hydrogen uptake capacity. Reports from Strobel et al. [55] and Nijkamp et al. [56] provided further experimental supports of the conclusion. Both of them observed the linear relationship between the uptake capacity and the specific surface area of carbon materials. The specific surface area of any carbon nanotubes or nanofibers cannot compete with super-activated carbon, and the storage at ambient temperature is too low to be practically utilized. That is why the storage of hydrogen in super-activated carbon cooled with liquid nitrogen is the only reasonable way to utilize the principle of physisorption. As shown in Figs. 5 and 6, the gravimetric density of the stored hydrogen is 10.8% (based on the weight of carbon) at 77 K and 6 MPa, and the volumetric density is 41 kg/m^3 [5]. The cryoadsorption method of hydrogen storage seems economically competitive because the cost of cool provided by liquid nitrogen is cheap, and the activated carbon can be used for long, and the boiling-off of hydrogen is replaced by the boiling-off of nitrogen. In comparison with activated carbon, the enhancement effect of the carbon nanotubes for hydrogen storage [57] is shown in Fig. 7. Clearly, carbon nanotubes cannot enhance hydrogen storage.

Recently, hydrogen storage with nanotubes of other materials was reported [58–60]. However, as long as the interaction between hydrogen molecules and the surface atoms of the material remains the Van der Waals force, specific surface area of the material is still the decisive factor of the storage capacity. A metal-organic framework of Zn_4O(1,4-benzenedicarboxylate)$_3$ was proposed as hydrogen storage material [61], which might trigger another research tide on storing hydrogen in this group of compounds. It was reported that hydrogen was absorbed at 298 K and the amount absorbed is proportional to

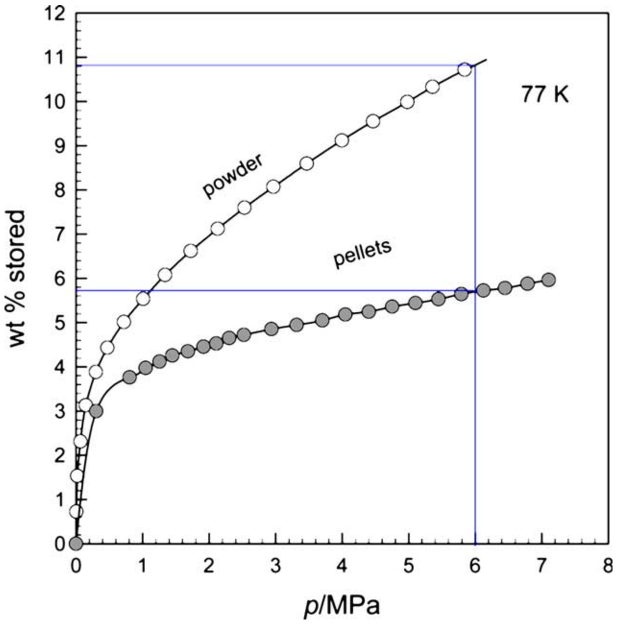


Fig. 5. Weight percentage of H_2 stored in activated carbon AX-21 powder and pellets [5].

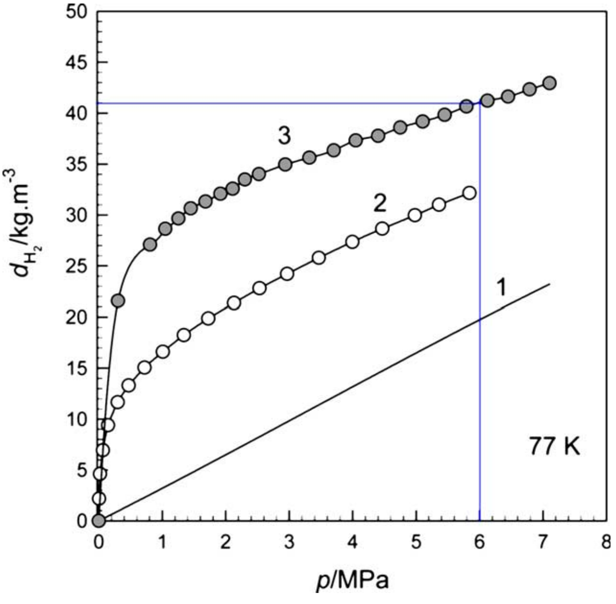


Fig. 6. Volumetric density of hydrogen in a vessel. 1, by compression only; 2, filled with carbon powder; 3, filled with carbon pellets [5].

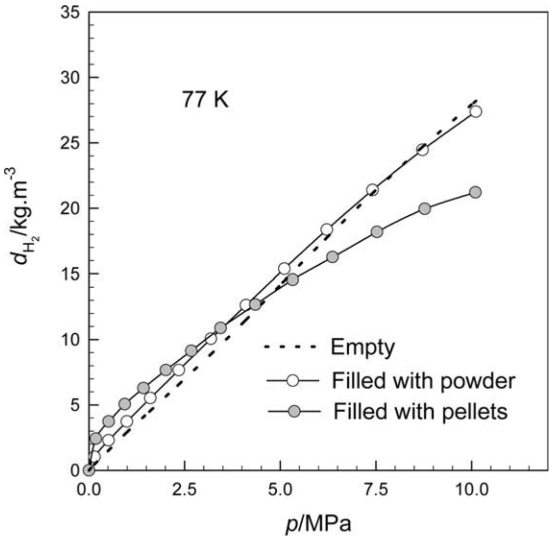


Fig. 7. Enhancement effect of carbon nanotube for hydrogen storage at 77 K [57].

the applied pressure. No saturation of absorption was found, which is very unlikely true for any kind of ab- or adsorption process. According to the lesson learnt from carbon nanotubes, such novel finding needs further verification, especially with the measurement in an expertised adsorption apparatus.

5. Metallic hydrides

Some metals and alloys absorb hydrogen and form hydrides. There are two classes of hydrides: metallic hydrides and complex hydrides. The main difference between them is the transition of metals to ionic or covalent compounds for the complex hydrides upon absorbing hydrogen. Some of the metallic hydrides of interest for the storage purpose are listed in Table 1 [7]. The prototype metallic hydrides are composed of two elements. The A element is usually a rare earth or an alkaline earth metal and tends to form a stable

Table 1
Most important families of hydrides forming in compounds

Intermetallic compound	Prototype	Hydrides	Structure
AB_5	$LaNi_5$	$LaNi_5H_6$	Haucke phase, hexagonal
AB_5	ZrV_2, $ZrMn_2$, $TiMn_2$	$ZrV_2H_{5.5}$	Laves phase, hexagonal or cubic
AB_3	$CeNi_3$, YFe_3	$CeNi_3H_4$	Hexagonal, $PuNi_3$-typ
A_2B_7	Y_2Ni_7,Th_2Fe_7	$Y_2Ni_7H_3$	Hexagonal, Ce_2Ni_7-typ
A_6B_{23}	Y_6Fe_{23}	$Ho_6Fe_{23}H_{12}$	Cubic, Th_6Mn_{23}-typ
AB	TiFe	$TiFeH_2$	Cubic, CsCl-or Ti_2Ni-typ
A_2B	Mg Ni, Ti_2Ni	Mg_2NiH_4	Cubic, $MoSi_2$-or Ti_2Ni-typ

hydride. The B element is often a transition metal and forms only unstable hydrides. Nickel is often used as B element since it is an excellent catalyst for the hydrogen dissociation.

Some metal hydrides absorb and desorb hydrogen at ambient temperature and near the atmospheric pressure, and the volumetric density of the hydrogen atoms present in the host lattice is extremely high. A volumetric density of 115 kg/m^3 was reached in $LaNi_5H_6$. However, all the reversible hydrides working around ambient temperature and atmospheric pressure consist of transition metals; therefore, the gravimetric hydrogen density is limited to less than 3 wt%, for example, the gravimetric density of hydrogen in $LaNi_5H_6$ is only 1.4%. Recent attention turns to the hydrides formed by light metals, and Mg becomes the focus. The formation of metal hydrides is an exothermic reaction. Significant heat is released during absorbing hydrogen and the same amount of heat is required in order for hydrogen released from the hydrides. More stable the hydride is, more heat is needed to desorb hydrogen. An amount of energy approximately 25% higher than the heating value of hydrogen is needed for the release of hydrogen from MgH_2. Although many efforts have been contributed to the Mg-based hydrides in recent years, it is still a challenge to find out an appropriate hydride of light metals.

6. Complex hydrides

Group I, II, and III elements, e.g. Li, Mg, B, Al, build a large variety of metal–hydrogen complexes. The number of hydrogen atoms per metal atom is 2 in many cases. This kind of complexes shows the highest volumetric density, 150 kg/m^3, in Mg_2FeH_6 and $Al(BH_4)_3$, and the highest gravimetric density at room temperature known today in $LiBH_4$ (18 wt%). $NaAlH_4$ can reversibly absorb/desorb hydrogen at moderate temperatures; therefore, received more attention [62–71]. $LiBH_4$ and $NaBH_4$ are also on the list of candidates [72–76]. Some researchers thought complex hydrides as the promising solution of the hydrogen storage problem may be because this group of material has not been well studied with respect to the behavior as a hydrogen carrier. The low dynamics of the hydrogen releasing process is a major problem. Unlike the metallic hydrides, hydrogen is released via cascade decompositions from the complex hydrides, and the step reactions call for different conditions. Therefore, there is a large difference between the theoretical and the practically attainable hydrogen capacities. Besides, significant changes in the particle morphology and elemental distribution were induced by hydrogen desorption [77]. Repeated absorption/desorption cycles have to be tested before the conclusion regarding the potential application being made. $Al(BH_4)_3$ also has very high gravimetric hydrogen density (17 wt%). It has a melting point of -65 °C and is liquid at room temperature. However, very little is known about it today.

7. Summary

Storage of hydrogen in a pressurized cylinder is not likely to be applied in the future due to the low density and high cost at high pressures. Liquid hydrogen could be applied if

the unit cost becomes comparable with gasoline, yet the inevitable boiling-off of liquid might be of concern. Metallic hydrides of heavy metals cannot get rid of the constraint of gravimetric density, and the relatively high temperature of ab- and desorption and the large amount of energy required for releasing hydrogen remain the barriers for the light metal hydrides. A confidential conclusion cannot be made for the complex hydrides before more works having been done. Physisorption of hydrogen on nanotubes/nanofibers of any materials seems hopeless for enhancing the hydrogen density due to the small surface area. Cryoadsorption of hydrogen on superactivated carbon of abundant slit-like micro-pores (<2 nm) is presently promising because it reaches the gravimetric density of more than 10 wt% and a reasonable volumetric density of 41 kg/m^3 at relatively low cost. However, to find out better technique of hydrogen storage remains a challenge facing us.

Acknowledgements

This work is subsidized by the Special Funds of Major State Basic Research Projects (G2000026404) and supported by the National Natural Science Foundation of China (grant number 20336020).

References

[1] Von Ardenne M. Effekte der Physik. Deutsch: Verlag Harry; 1990 p. 712–5.
[2] Brunauer S, Emmett PH, Teller E. Adsorption of gases in multimolecular layers. J Am Chem Soc 1938;60: 309–19.
[3] Beebe BA, Biscoe J, Smith WR, Wendell CB. Heats of adsorption on carbon black I. J Am Chem Soc 1947; 69:95–101.
[4] Zhou YP, Zhou L. Utility study of conventional adsorption equations for modeling isotherms in a wide range of temperature and pressure. Sep Sci Technol 1998;33:1787–802.
[5] Zhou L, Zhou YP, Sun Y. Enhanced storage of hydrogen at the temperature of liquid nitrogen. Int J Hydrogen Energy 2004;29:319–22.
[6] Dillon AC, Jones KM, Bekkedahl TA, Kiang CH, Bethune DS, Heben MJ. Storage of hydrogen in single-walled carbon nanotubes. Nature 1997;386:377–9.
[7] Zuttel A. Hydrogen storage methods and materials. Naturwissenschaften 2004;91:157–72.
[8] Hirscher M, Becher M, Haluska M, Dettlaff-Wegbikowska U, Quintel A, Duesberg GS, et al. Hydrogen storage in sonicated carbon materials. Appl Phys A 2001;72:129–32.
[9] Chambers A, Park C, Terry R, Baker K. Hydrogen storage in graphite nanofibers. J Phys Chem B 1998; 102(22):4254–6.
[10] Ahn CC, Ye Y, Ratnakumar BVC, Witham RC, Bowman Jr RC, Fultz B. Hydrogen desorption and adsorption measurements on graphite nanofibers. Appl Phys Lett 1998;73:3378–80.
[11] Liu C, Fan YY, Liu M, Cong HT, Cheng HM, Dresselhaus MS. Hydrogen storage in single-walled carbon nanotubes at room temperature. Science 1999;286(5442):1127–9.
[12] Fan YY, Liao B, Liu M, Wei YL, Lu MQ, Cheng HM. Hydrogen uptake in vapor-grown carbon nanofibers. Carbon 1999;37:1649–52.
[13] Fan YY, Liu M, Cheng HM. Studies on the hydrogen uptake by carbon nanofibers Proceedings of the Fourth National Symposium on Novel Carbon Materials 1999 [in Chinese], p. 582–7.
[14] Mao ZQ, Xu CL, Yan J, Liang J, Sun GM, Wei BQ, et al. Preliminary study on the hydrogen storage capacity of carbon nanofibers. Novel Carbon Mater 2000;15:64–7 [in Chinese].

[15] Chen P, Wu X, Lin J, Tan KL. High H2 uptake by alkali-doped carbon nanotubes under ambient pressure and moderate temperatures. Science 1999;285:91.
[16] Ye Y, Ahn CC, Witham C, Fultz B, Liu J, Rinzler AG, et al. Hydrogen adsorption and cohesive energy of single-walled carbon nanotubes. Appl Phys Lett 1999;74:2307.
[17] Wu XB, Chen P, Lin J, Tan KL. Hydrogen uptake by carbon nanotubes. Int J Hydrogen Energy 2000;25: 261–5.
[18] Cheng HM, Liu C, Fan YY, Li F, Su G, Cong HT, et al. Synthesis and hydrogen storage of carbon nanotubes and single walled carbon nanotubes. Z Mrtallkd 2000;91:306–10.
[19] Li XS, Zhu HW, Ci LJ, Xu CL, Mao ZQ, Wei BQ, et al. Hydrogen uptake by graphitized multi-walled carbon nanotubes under moderate pressure and at room temperature. Carbon 2001;39:2077–88.
[20] Li XS, Zhu HW, Mao ZQ, Wei BQ, Liang J. Effects of structure and surface properties on carbon nanotubes' hydrogen storage characteristics. Chin Sci Bull 2001;46:1358–60.
[21] Poirier E, Chahine R, Bose TK. Hydrogen adsorption in carbon nanostructures. Int J Hydrogen Energy 2001; 26:831–5.
[22] Zhu HW, Chen A, Mao ZQ, Xu CL, Xiao X, Wei BQ, et al. The effect of surface treatments on hydrogen storage of carbon nanotubes. J Mater Sci Lett 2002;19:1237–9.
[23] Huang WZ, Zhang XB, Tu JP, Chen CP. The effect of pre-treatments on hydrogen adsorption of multi-walled carbon nanotubes. Mater Chem Phys 2002;78:144–8.
[24] Zuttel A, Sudan P, Mauron P, Kiyobayashi T, Emmenegger C, Schlapbach L. Hydrogen storage in carbon nanostructures. Int J Hydrogen Energy 2002;27:203–12.
[25] Bhabendra K, Pradhan GU, Sumanaskera KWA, Hugo ER, Keith AW, Eklund PC. Experimental probes of the molecular hydrogen–carbon nanotube interaction. Physica B 2002;323:115–21.
[26] Wang QK, Zhu CC, Liu WH, Wu T. Hydrogen storage by carbon nanotube and their films under ambient pressure. Int J Hydrogen Energy 2002;27:497–500.
[27] Hirscher M, Becher M, Haluska M, Becher M, Haluska A, Quintel V, et al. Hydrogen storage in carbon nanostructures. J Alloys Comp 2002;330–332:654–8.
[28] Pradhan BK, Harutyunyan A, Stojkovic D, Zhang P, Cole MW, Crespi V, et al. Large cryogenic storage of hydrogen in carbon nanotubes at low pressure. Mater Res Soc Symp Proc 2002;706:Z10.3.1–Z10.3.6.
[29] Zuttel A, Nutzenadel C, Sudan P, Mauron P, Emmenegger C, Rentsch S, et al. Hydrogen sorption by carbon nanotubes and other carbon nanostructures. J Alloys Comp 2002;330–332:676–82.
[30] Smith MR, Bittner EW, Bockrath BC. Activating single walled carbon nanotubes for hydrogen adsorption. Preprints Symp Am Chem Soc Div Fuel Chem 2002;47:784–5.
[31] Lupu D, Biris AR, Misan I, Lupsa N, Biris AS, Buzatu DA, et al. Growth of nanoscale carbon structures and their corresponding hydrogen uptake properties. Particulate Sci Technol 2002;20:225–34.
[32] Gabis IE, Evard EA, Gordeev SK, Ekstrom T. Carbon nanomaterial for hydrogen uptake and storage. Hydrogen materials science and chemistry of metal hydrides NATO Science Series, II: mathematics, physics and chemistry, vol. 71. Dordrecht: Kluwer Academic Publishers; 2002 p, 383–90.
[33] Pradhan BK, Harutyunyan AR, Eklund PC. Hydrogen storage in carbon nanomaterials at low temperature. Preprints Symp Am Chem Soc Div Fuel Chem 2002;47:477–80.
[34] Tang CC, Bando Y, Ding XX, Qi SR, Golberg D. Catalyzed collapse and enhanced hydrogen storage of BN nanotubes. J Am Chem Soc 2002;124(49):14550–1.
[35] Zhu HW, Li XS, Ci LJ, Xu CL, Wu DH, Mao ZQ. Hydrogen storage in heat-treated carbon nano-fibers prepared by the vertical floating catalyst method. Mater Chem Phys 2003;78:670–5.
[36] Kajiura H, Tsutsui S, Kadono K, Ata M, Murakami Y. Hydrogen storage capacity of commercially available carbon materials at room temperature. Appl Phys Lett 2003;82:1105–7.
[37] Lueking A, Yang RT. Hydrogen storage in carbon nanotubes: residual metal content and pretreatment temperature. AIChE J 2003;49:1556–8.
[38] Gao H, Wu XB, Li JT, Wu GT, Lin JY, Wu K, et al. Hydrogen adsorption of open tipped insufficiently graphitized multiwalled carbon nanotubes. Appl Phys Lett 2003;83:3389–91.
[39] Hanada K, Shiono H, Matsuzaki K. Hydrogen uptake of carbon nanofiber under moderate temperature and low pressure. Diam Rel Mater 2003;12:874–7.
[40] Hou PX, Xu ST, Ying Z, Yang QH, Liu C, Cheng HM. Hydrogen adsorption/desorption behavior of multi-walled carbon nanotubes with different diameters. Carbon 2003;41:2471–6.

[41] Shaijumon MM, Ramaprabhu S. Synthesis of carbon nanotubes by pyrolysis of acetylene using alloy hydride materials as catalysts and their hydrogen and adsorption studies. Chem Phys Lett 2003;374:513–20.
[42] Tibbetts GG, Meisner CP, OLK CH. Hydrogen storage capacity of carbon nanotubes, filaments, and vapor-grown fibers. Carbon 2001;39:2291–301.
[43] Shiraishi M, Takenobu T, Ata M. Gas–solid interactions in the hydrogen/single-walled carbon nanotubes system. Chem Phys Lett 2003;367:633–6.
[44] Loutfy RO, Moravsky A, Franco A, Veksler E. In: Osawa E, editor. Physical hydrogen storage on nanocarbon materials. Perspectives of fullerene nanotechnology. Dordrecht, Netherlands: Kluwer Academic Publishers; 2002.
[45] Kiyobayashi T, Hiroyuki T, Tanaka H, Takeichi N, Zuttel A, Schlapbach L, et al. Hydrogen adsorption in carbonaceous materials—how to determine the storage capacity accurately. J Alloys Comp 2002;330–332: 666–9.
[46] Ritschel M, Uhlemann M, Gutfleisch O, Leonhardt A, Graff A, Taschner C, et al. Hydrogen storage in different carbon nanostructures. Appl Phys Lett 2002;80:2985–7.
[47] Zhou YP, Feng K, Sun Y, Zhou L. Adsorption of hydrogen on multiwalled carbon nanotubes at 77 K. Chem Phys Lett 2003;380(5–6):526–9.
[48] Leung WB, March NH, Motz H. Primitive phase diagram for hydrogen. Phys Lett A 1976;56:425–6.
[49] Ma Y, Xia Y, Zhao M, Wang R, Mei L. Effective hydrogen storage in single-wall carbon nanotubes. Phys Rev B 2001;63:115422.
[50] Zhou L, Zhou YP, Sun YA. Comparative study of hydrogen adsorption on superactivated carbon versus carbon nanotubes. Int J Hydrogen Energy 2004;29:475–9.
[51] Zhou YP, Zhou L. Experimental study on high pressure adsorption of hydrogen on activated carbon. Sci China (Ser B) 1996;39:598–607.
[52] Zhou L, Zhou YP. Linearization of adsorption isotherms for high pressure applications. Chem Eng Sci 1998; 53:2531–6.
[53] Zhou L, Zhou YP. A mathematical method for the determination of absolute adsorption from experimental isotherms of supercritical gases. Chin J Chem Eng 2001;9:110–5.
[54] Zhou L, Zhang JS, Zhou YP. A simple isotherm equation for modeling the adsorption equilibria on porous solids over wide range temperatures. Langmuir 2001;17:5503–7.
[55] Strobel R, Jorisen L, Schliermann T, Trapp V, Schutz W, Bohmhammel K, et al. Hydrogen adsorption on carbon materials. J Power Sources 1999;84:21.
[56] Nijkamp MG, Raaymakers JE, van Dillen AJ, de Jong KP. Hydrogen storage using physisorption—materials demands. Appl Phys A 2001;72:619.
[57] Zhou YP, Feng K, Sun Y, Zhou L. A brief review on the study of hydrogen storage in terms of carbon nanotubes. Prog Chem (Chin) 2003;15:345–50.
[58] Chen P, Xiong Z, Luo J, Lin J, Tan KL. Interaction of hydrogen with metal nitrides and imides. Nature 2002; 420:302–4.
[59] Chen J, Li SL, Tao L. Novel hydrogen storage properties of MoS2 nanotubes. J Alloys Comp 2003;356–357:413–7.
[60] Oku T, Kuno M. Synthesis, argon/hydrogen storage and magnetic properties of boron nitride nanotubes and nanocapsules. Diam Rel Mater 2003;12:840–5.
[61] Rosi NL, Eckert J, Eddaoudi M, Vodak DT, Kim J, O'Keeffe M, et al. Hydrogen storage in microporous metal-organic frameworks. Science 2003;300:1127–9.
[62] Gross KJ, Thomass GJ, Jensen CM. Catalyzed alanates for hydrogen storage. J Alloys Comp 2002;330–332: 683–90.
[63] Bogdanovic B, Schwickardi M. Ti-doped alkali metal aluminum hydrides as potential novel reversible hydrogen storage materials. J Alloys Comp 1997;253–254:1–9.
[64] Bogdanovic B, Brand RA, Marjanovic A, Schwikardi M, Tolle J. Metal doped sodium aluminum hydrides as potential new hydrogen storage materials. J Alloys Comp 2000;302:36–58.
[65] Tolle J. PhD Thesis. Germany: Ruhr-Universitat Bochum; 1998.
[66] Jensen CM, Zidan RA, Mariels N, Hee AG, Hagen C. Advanced titanium doping of sodium aluminum hydride: segue to a practical hydrogen storage material? Int J Hydrogen Energy 1999;24:461–5.

[67] Zidan RA, Takara S, Hee AG, Jensen CM. Hydrogen cycling behavior of zirconium and titanium–zirconium-doped sodium aluminum hydride. J Alloys Comp 1999;285:119–22.
[68] Zaluska A, Zaluski L, Strom-Oslen JO. Sodium alanates for reversible hydrogen storage. J Alloys Comp 2000;298:125–34.
[69] Huot J, Boily S, Guther V, Schulz R. Synthesis of Na3A1H6 and Na2LiAiH6 by mechanical alloying. J Alloys Comp 1999;283:304–6.
[70] Zaluski L, Zaluska A, Strom-Olsen JO. Hydrogenation properties of complex alkali metal hydrides fabricated by mechano-chemical synthesis. J Alloys Comp 1999;290:71–8.
[71] Lewandowski B, Seidl T, Takara S, Sun D, Jensen C. Dissociation–reassociation kinetics of catalytically enhanced NaA1H4 Presentation MH2000 Symposium. Australia: Noosa; 2000.
[72] Schlesinger HJ, Brown HC. Metallo borohydrides. III. Lithium borohydride. J Am Chem Soc 1940;62: 3429–35.
[73] Schlesinger HJ, Brown HC, Hoekstra HR, Rapp LR. Reactions of diborane with alkali metal hydrides and their addition compounds. New syntheses of borohydrides. Sodium and potassium borohydrides. J Am Chem Soc 1953;75:199–204.
[74] Goerring D. Ger. Pat. 1, 077,644; Dec.27, 1958.
[75] Schrauzer GN. Uber ein Periodensystem der Metallboranate. Naturwissenschaften 1955;42:438.
[76] Zuttel A, Wenger P, Rensch S, Sudan P, Mauron P, Emmenegger C. LiBH4 a new hydrogen storage material. J Power Sources 2003;118:l–7.
[77] Thomass GJ, Gross KJ, Yang NYC, Jensen C. Microstructural characterization of catalyzed NaA1H4. J Alloys Comp 2002;330–332:702.